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REMOTE FIBER OPTIC SENSOR FOR GASEOUS AND LIQUID
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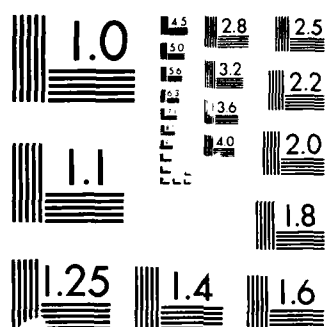
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AD-A195 718

REPORT N00014-87-C-0859(F)

REMOTE FIBER OPTIC SENSOR FOR GASEOUS AND
LIQUID ENVIRONMENTS BASED ON SURFACE ENHANCED
RAMAN SPECTROSCOPY (SERS) - PHASE I

Principal Investigator - Michael M. Carrabba
Program Manager - R. David Rauh

EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

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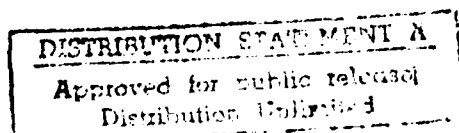
March, 1988

Final Report for Period 16 September 1987 - 28 February 1988
Contract No. N00014-87-C-0859

Prepared for

OFFICE OF NAVAL RESEARCH
Department of the Navy
800 North Quincy Street
Arlington, Virginia 22217

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**SMALL BUSINESS INNOVATION RESEARCH PROGRAM
PHASE 1 — FY 1987
PROJECT SUMMARY**

Military Department/Agency Navy

EIC Laboratories, Inc.
111 Downey Street
Norwood, MA 02062

Dr. Michael M. Carrabba, Senior Scientist (Principal Investigator)
Dr. R. David Rauh, Director of Research (Program Director)

Technical Abstract (Limit your abstract to 200 words with no classified or proprietary information/data.)

There is a universal need within defense-related operations for chemical sensing. It is most desirable for the detector (i.e. probe) to operate in situ and to produce information on chemical composition in real time with a high degree of sensitivity (ppb or less). It is the goal of this work to develop a "universal" remote sensor for organic and inorganic compounds in both gaseous and liquid environments, based on surface enhanced Raman spectroscopy (SERS). The SERS signal is observed as the enhanced Raman spectrum of molecules adsorbed onto certain active metal substrates.

The goal of Phase I was to determine the feasibility of using SERS in gas phase sensing. It was found that, while some roughened metals show high SERS activity in the liquids, they tend to show low activity for molecules in the vapor phase. However, high gas phase SERS activity was observed for electrochemically oxidized Ag and Au substrates, a major finding of the investigation. Oxide surfaces were demonstrated for the reversible gas phase sensing of alcohols (ethanol and methanol and mixtures), aromatics (benzene), heterocycles (pyridine), a chemical agent simulant (DMMP), formaldehyde and hydrazine (a rocket fuel component, down to 4 ppm). Similar sensitivities were obtained in both air and inert atmospheres.

Recent results in our laboratory also confirm the feasibility of using silica fiber optics for both excitation and returning the scattered light to the detector, and the achievement of parts per trillion sensitivity for organics in aqueous environments. The technique could be developed into instrumentation for a variety of sensing applications, including groundwater monitoring, cabin atmosphere monitoring, and environmental sensors for undersea and terrestrial robotic explorers.

Fiber Optic, Sensor, Raman, Air Quality, Groundwater, Environment, "13"

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ACKNOWLEDGMENTS

This work was carried out under the direction of Dr. R. David Rauh, Program Manager, and Dr. Michael M. Carrabba, Principal Investigator. We would like to thank Dr. Martin W. Rupich and Mr. Peter J. Marren for their contributions to the experimental aspects of this program. We would also like to thank Mr. Robert B. Edmonds for his technical discussions.

DESCRIPTION OF PROGRESS

The purpose of this program is to develop "universal" chemical sensors for detecting and identifying a wide variety of molecular species in both gaseous and liquid environments. Defense-related applications for such chemical sensors include chemical warfare agent detection, robotics (sensing of smell and taste), hazardous waste monitoring, environmental monitoring and control of cabin atmospheres, and process control monitoring. Ideally, a chemical sensor should produce information in real time that is both selective and sensitive. Currently, experimental chemical sensors such as chemiresistors, SAW devices, CHEMFETS and optrodes (fiber optic chemical sensors) [1] are specific to only one compound or class of compounds and are generally not applicable to the identification of previously unknown contaminants.

Our approach has been to sample chemical species in the environment (liquid or gaseous) by adsorption onto metal surfaces, and then to identify the adsorbates by vibrational spectroscopic techniques. Recent work in our laboratory [2-4] has demonstrated the feasibility of using fiber optic based Surface Enhanced Raman Spectroscopy (SERS) of adsorbates on metal surfaces for the detection and analysis of organic constituents in aqueous environments. Advantages of fiber optics include in situ sampling of remote or adverse environments, low cost, small size of sampling probe, real time analysis and the ability of using a central detection facility, and reduced electromagnetic interference. Raman techniques such as SERS utilize visible light to obtain vibrational spectra, and hence are well suited to a fiber optic approach. Raman techniques also enable measurements in aqueous media, which absorb strongly in the infrared. Finally, SERS improves greatly on the low sensitivity associated with conventional Raman spectroscopy.

The Phase I program has been directed at demonstrating the feasibility of using SERS for the analysis of low levels of organic contaminants in gaseous environments. Until now, SERS has been primarily associated with the liquid phase. The SERS phenomenon was first reported by Fleischmann and co-workers in 1974 [5], who described a very large enhancement of the Raman signal from pyridine when adsorbed onto an electrochemically roughened Ag surface. Quantitative studies of Raman scattering from molecules adsorbed onto electrochemically roughened substrates of highly reflective metals indicate that the SERS enhancement factor is approximately 10^6 compared to the signal of adsorbates on non-active or smooth surfaces [6].

Although numerous reports have dealt with the theory of SERS [7,8], only a few analytical studies employing SERS have appeared in the literature [9-15]. One example reported by EIC Laboratories [2] determined a detection limit on Ag electrodes of 8.5 picograms. Another example by Vo-Dinh et al. [9-11,15] employed Ag-coated microspheres embedded in either a glass or cellulose substrate. Using an ex situ spotting technique to concentrate the sample on the microspheres, they were able to detect $<10^{-11}$ g of several different organic compounds, which is in the 10^9 to 10^{10} molecule range and they were also able to resolve mixtures.

The possibility of using SERS as an in situ technique for the resolution of mixtures into its different Raman-active components has also recently been demonstrated at EIC [2] in aqueous media. In this case, the SERS-related phenomena which are chemically specific, such as the adsorption of organic molecules on metal substrates and the potential dependence of electrosorption, were used to distinguish mixtures of organic compounds. Figure 1 is an example of the ability to distinguish a mixture of pyridine and quinoline with the SERS technique.

Previous work on gas phase SERS has been, for the most part, restricted to ultrahigh vacuum techniques [8]. As a result, the following questions were addressed in Phase I:

- Can typical organic vapors be detected by SERS under normal atmospheric conditions?
- Can electrochemically prepared surfaces be used as gas phase SERS substrates under normal atmospheric conditions?
- Can electrochemically prepared surfaces show structural and chemical selectivity of adsorption?
- Does the SERS signal reflect the concentration of the organic vapor?
- Can the substrates that show strong adsorption properties be renewed by heating?
- Can a mixture of organic vapors be characterized by SERS under normal atmospheric conditions?

Experimental Details

The experiments were conducted at the EIC Laboratories, Inc. Raman facility. This instrumentation includes a triple spectrograph (1877C Triplemate), a tunable excitation filter (Model 1450), a polarization scrambler, and a Raman sample compartment (Model 1439T) from Spex Industries. The signal is detected with an EG&G Optical Multichannel Analyzer (Model 1460) with an intensified diode array detector (Model 1420R-1024-SG) for high speed data acquisition (approximately 1 second for a complete spectrum). The excitation source is either a Coherent Argon Ion (Model 70-4) or a Coherent dye laser (Model 599-01). The dye laser was operated in the region of 570 to 630 nm while the argon laser has various laser lines between 450 and 525 nm.

The metal sensing substrates were prepared from 1 mm diameter polycrystalline wire. The tip of the wire was wrapped with a resistive heating element and sealed into a 6 mm glass tube along with a thermocouple. The metal surfaces were mechanically polished to a mirror finish using 0.3 and 0.05 μm alumina. After polishing, the surfaces were rinsed in doubly distilled water. Immediately before use, each metal surface was electrochemically roughened by potentiostatic cycling in 0.1M KCl. Gold electrodes were cycled 25 times at 50 mV/sec between -0.6 and 1.2V (vs. SCE). Silver electrodes were cycled 5

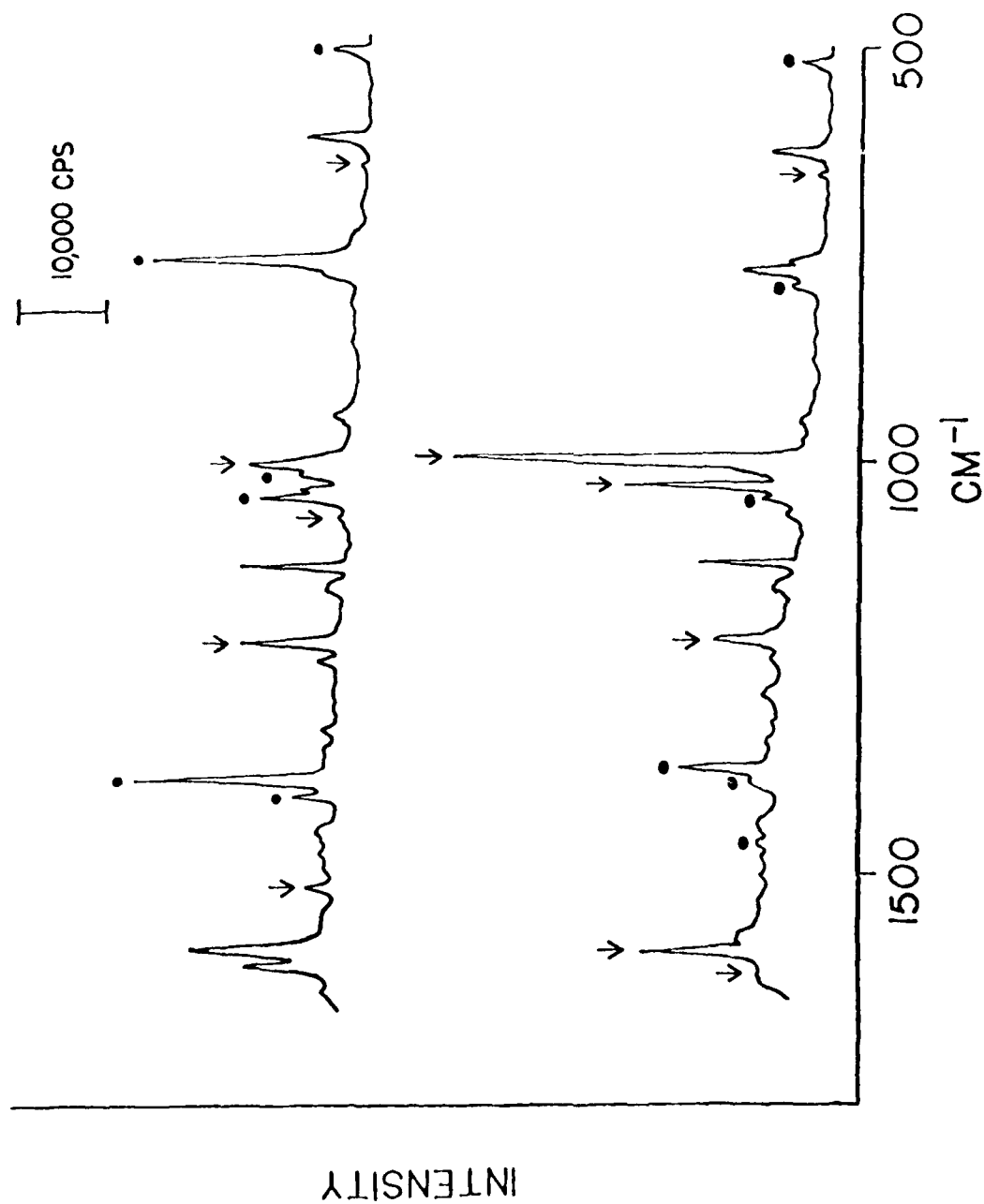


Fig. 1. SERS spectra of a mixture of pyridine and quinoline on an Ag electrode at a potential of -1.0 (top) and -0.6 (bottom) volts (vs. SCE). The excitation wavelength is 514.5 nm. The arrows and dots indicate the major peaks due to pyridine and quinoline, respectively.

times between -0.6 and 0.2V (vs. SCE) at 20 mV/sec. The potentiostatic cycling was stopped at cathodic potentials with both silver and gold electrodes. The electrodes were removed from the 0.1M KCl, rinsed in doubly distilled water and air dried.

Gold oxide surfaces were prepared by potentiostating previously roughened gold electrodes in 1M H₂SO₄ at 1.1V (vs. SCE) for 10 minutes. Silver oxide surfaces were prepared by potentiostating previously roughened silver electrodes in 1M KOH at 0.9V (vs. SCE) for 10 minutes. The oxide electrodes were removed from the solutions, rinsed with doubly distilled water and air dried before use.

All electrochemical experiments were carried out with a Princeton Applied Research Model 273 potentiostat interfaced to an IBM Personal Computer. The metal sensing substrates were incorporated into a custom SERS cell. The cell allows for the flowing of the gases of interest. Unless noted otherwise, The test gases were typically prepared by flowing a carrier gas through a bubbler containing an organic liquid.

Results

The major finding of the Phase I work was that numerous organic compounds including pyridine, toluene, benzene, formaldehyde, hydrazine, methanol, ethanol and dimethyl methylphosphonate (DMMP) are observable with SERS techniques in the gas phase under normal atmospheric conditions. The reason for this success was the discovery that gas phase SERS activity is much improved on some substrates in the presence of an electrochemically formed oxide layer compared to the electrochemically roughened bare metal employed in liquid phase detection.

Figure 2 shows a SERS spectrum of pyridine on an electrochemically prepared Ag surface. The carrier gas was air. The spectrum displays the same peaks as observed in solution or in ultra high vacuum. As indicated in Figure 2, the peak intensity decreases as pyridine is purged from the system and increases when the pyridine/air mix is reintroduced. This indicates that the adsorption of pyridine on a Ag surface is a dynamic physisorptive process and thus Ag is a naturally renewable surface for this molecule. This is an important aspect, particularly for applications to gas sensors.

Pyridine, and presumably structurally related compounds, adsorb onto a variety of metal and metal oxide surfaces through the lone pair of electrons on the nitrogen. Figure 3 shows the SERS spectra of pyridine in air on gold and gold oxide substrates. It is interesting to note that there is a slight shift in the peak positions between the two substrates and the adsorption on gold oxide results in a large signal enhancement. In comparison, pyridine shows no adsorption on extremely basic silver oxide surfaces. This result is indicative of the structural selectivity that can be achieved on different substrates.

The adsorption of pyridine on gold oxide, in contrast to Ag, is not a dynamic process at 20°C. However, as illustrated in Figure 4, the adsorbed pyridine

PYRIDINE ON SILVER

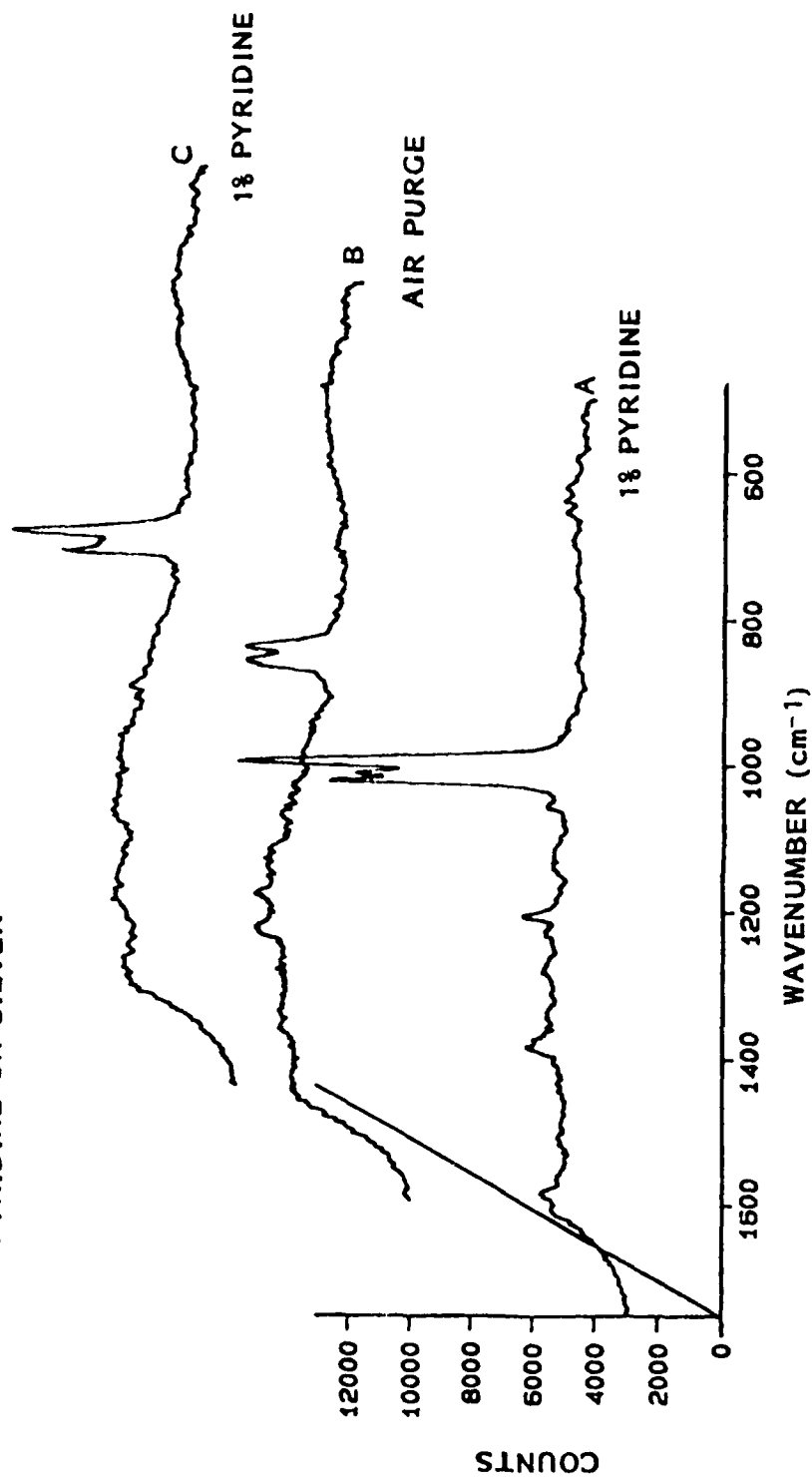


Fig. 2. SERS spectra of pyridine on an electrochemically prepared Ag surface at an excitation wavelength of 575 nm. Spectrum A is the initial signal, spectrum B was obtained after purging the sensor with air, and spectrum C was obtained after reexposure of the sensor to the pyridine-air mixture.

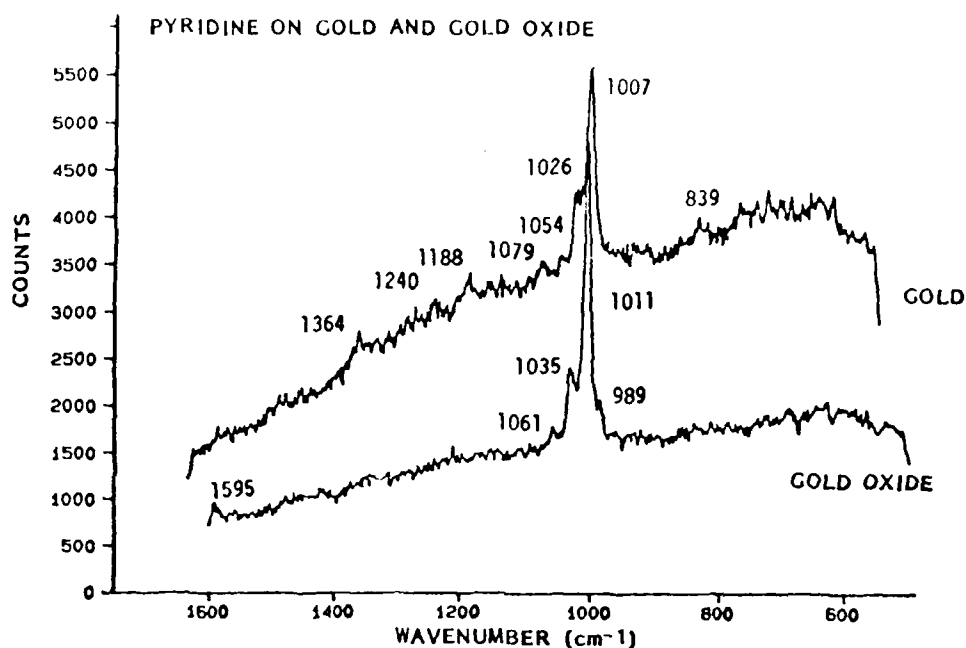


Fig. 3. SERS spectra of pyridine in air on a gold and gold oxide substrate at an excitation wavelength of 625 nm.

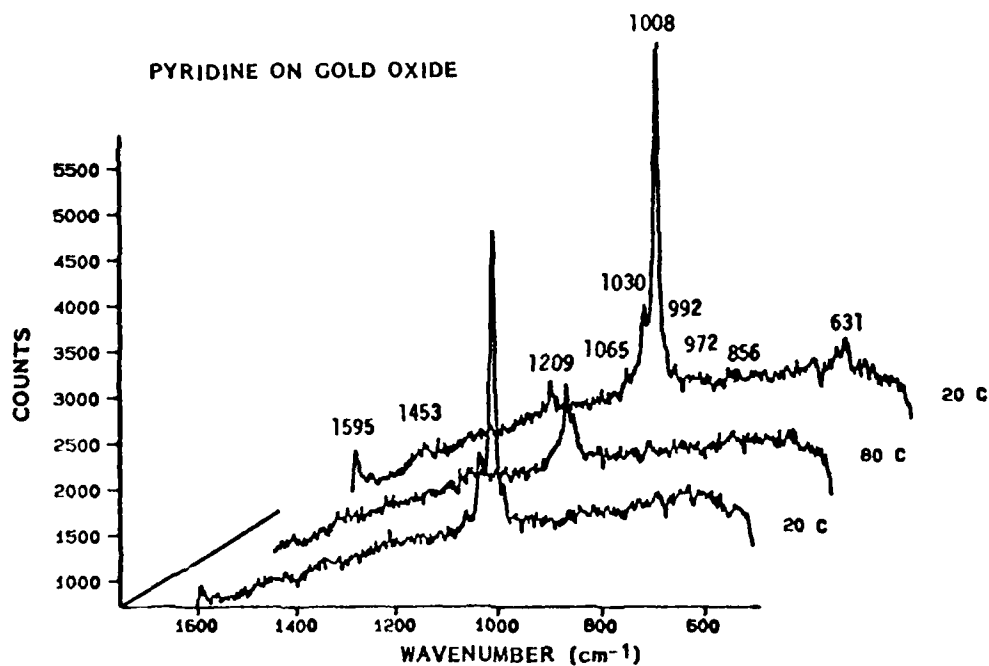
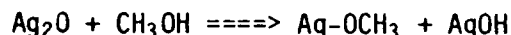


Fig. 4. SERS spectra of pyridine in air on a gold oxide substrate as a function of the substrate temperature at an excitation wavelength of 625 nm.

thermally desorbs from the gold oxide at approximately 80°C. Subsequent cooling of the substrate in the gas stream results in the reappearance of the original signal. Figure 5 shows the SERS spectra of benzene on gold oxide at various temperatures. The adsorbed benzene is desorbed from the gold oxide surface at lower temperatures than pyridine, which reflects the weaker strength of the adsorption interaction. This provides a degree of selectivity, since in a mixture of benzene and pyridine the benzene should be removed from the surface at lower temperatures.

Figure 6 compares the SERS spectra of methanol and ethanol on silver oxide. The methanol on the silver oxide surface was not in a dynamic equilibrium with the silver oxide surface, and we were unable to thermally remove the adsorbate at temperatures below 200°C. In contrast, the adsorption of methanol on gold oxide is reversible process at 20°C. Figure 7 shows the spectrum of methanol on gold oxide along with a response plot showing the peak intensity of the major peak as a function of a step change in the methanol concentration. The time to reach 90% of maximum response following a step change in concentration is 33 seconds for both increasing and decreasing concentrations. The differences in the methanol signal observed on the two substrates are believed to arise from differences in the oxidizing strengths and basicities of the individual surfaces. The irreversible adsorption of methanol on silver oxide, which is the most basic and the strongest oxidant of the substrates we examined, is believed to result from the decomposition of methanol on the silver oxide surface according to



The peaks at 682, 1049 and 1530 cm^{-1} can probably be assigned to the products of the above reaction. However, this has not been verified. In contrast, the adsorbed methanol is not readily decomposed on gold oxide, which is much less basic and not a strong oxidizing agent. In our experiments, methanol was not detected at all on unoxidized, roughened silver and gold surfaces.

Figure 8 shows the SERS spectra of formaldehyde on silver oxide at several substrate temperatures. A comparison (Figure 9) of the normal Raman spectrum (neat solution) and the SERS spectra on silver oxide and gold oxide of formaldehyde shows a shift in the general vibrational pattern of approximately 200 cm^{-1} . This also shows the occurrence of a chemisorption process of the formaldehyde on the silver oxide. It is interesting to note that as the formaldehyde is removed by heating, it is at least partially converted to a product with the same vibrational spectrum as the adsorbate formed with methanol.

In contrast to the other molecules studied, hydrazine appears to be a dynamic, reversible adsorption process with the silver oxide surface. Figure 10 shows the hydrazine spectrum (4 ppm) before and after an air purges along with a plot of the signal from the 802 cm^{-1} peak to step changes in the hydrazine concentration. The spectra indicate that peaks rise (678, 802, 1276 cm^{-1}) in the presence of hydrazine while other peaks, due to reaction products, decrease (601, 909 cm^{-1}). This is probably due to the ability of the hydrazine to displace reaction products from the surface. The response time to reach 90% of the maximum signal was approximately 15 seconds following a step change in concentration. Hydrazine was also observed on gold surfaces, but the results seem to indicate an irreversible adsorption process.

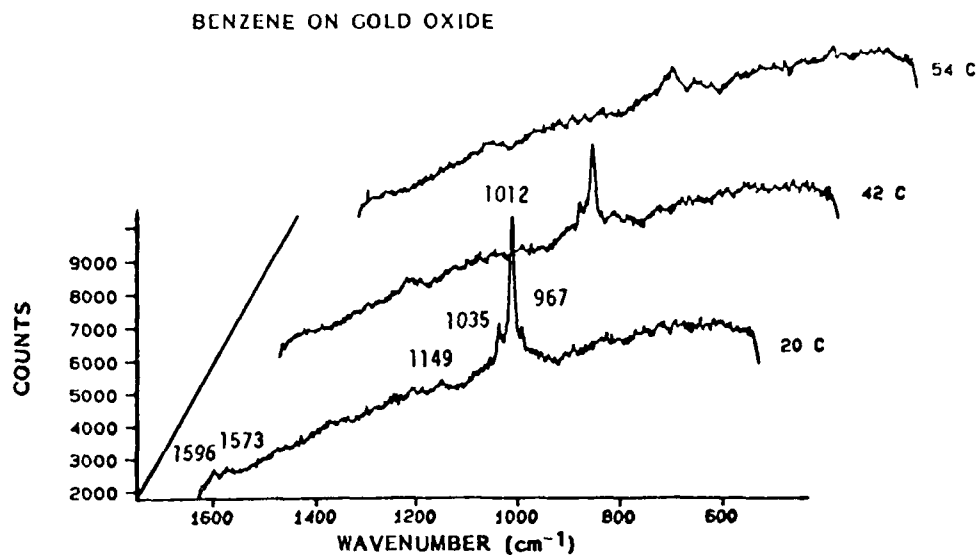


Fig. 5. SERS spectra of benzene in air on a gold oxide substrate as a function of the substrate temperature at an excitation wavelength of 625 nm.

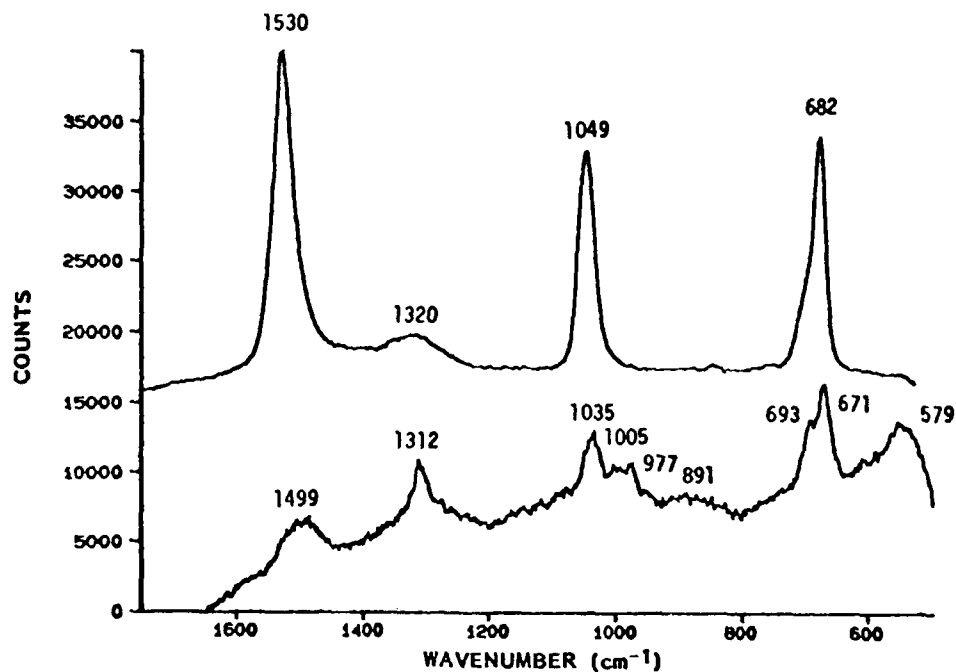


Fig. 6. SERS spectra of methanol-air and ethanol-air vapor samples on silver oxide substrate at an excitation wavelength of 575 nm.

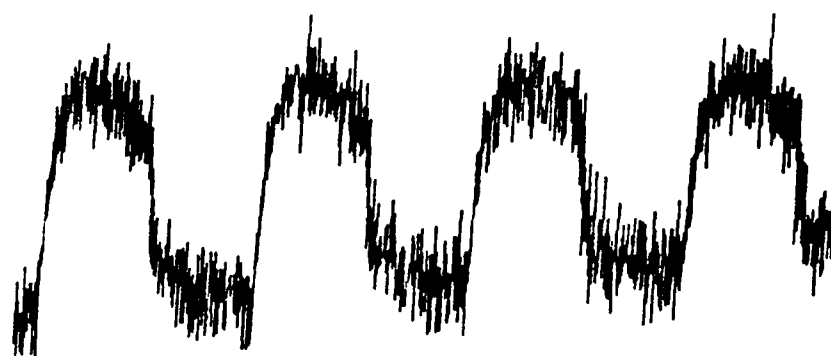
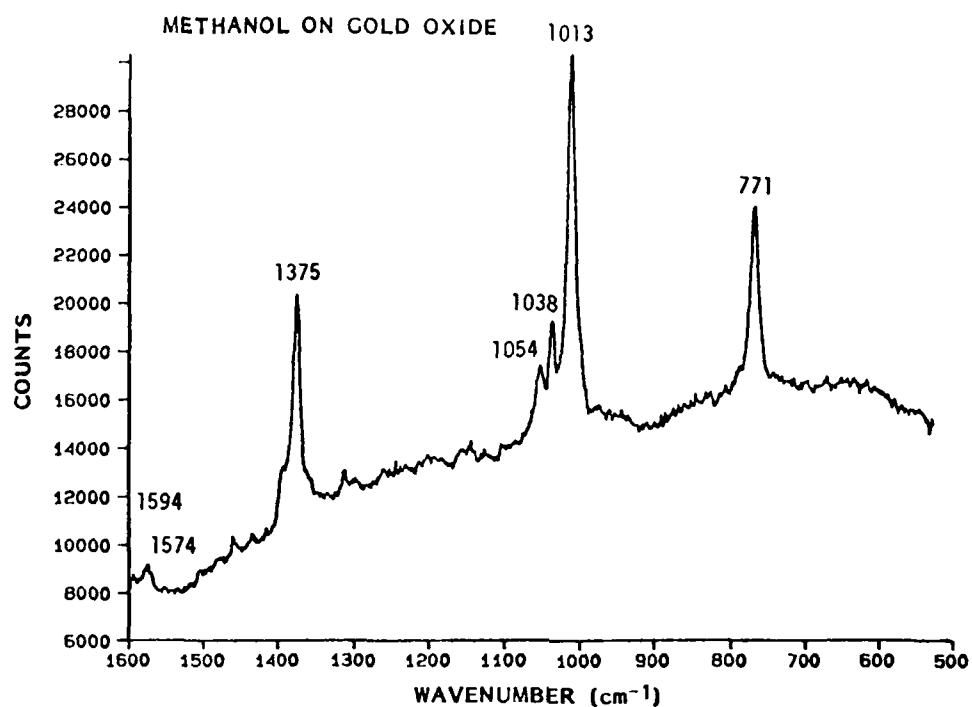


Fig. 7. SERS spectrum (top) of a methanol-air gas sample on a gold oxide substrate at an excitation wavelength of 625 nm. The bottom curve shows the intensity of the 1010 cm^{-1} peak as the sample gas was alternately switched from methanol-air mixtures to air.

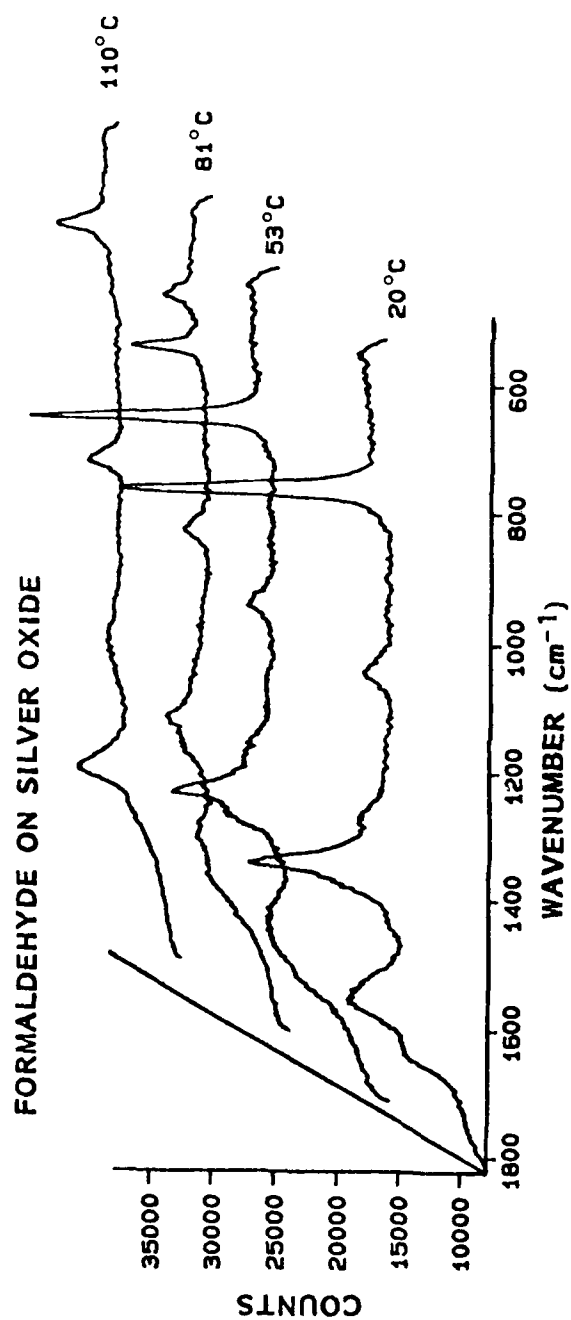


Fig. 8. SERS spectra of formaldehyde-air gas samples on a silver oxide substrate as a function of substrate temperature at an excitation of 575 nm.

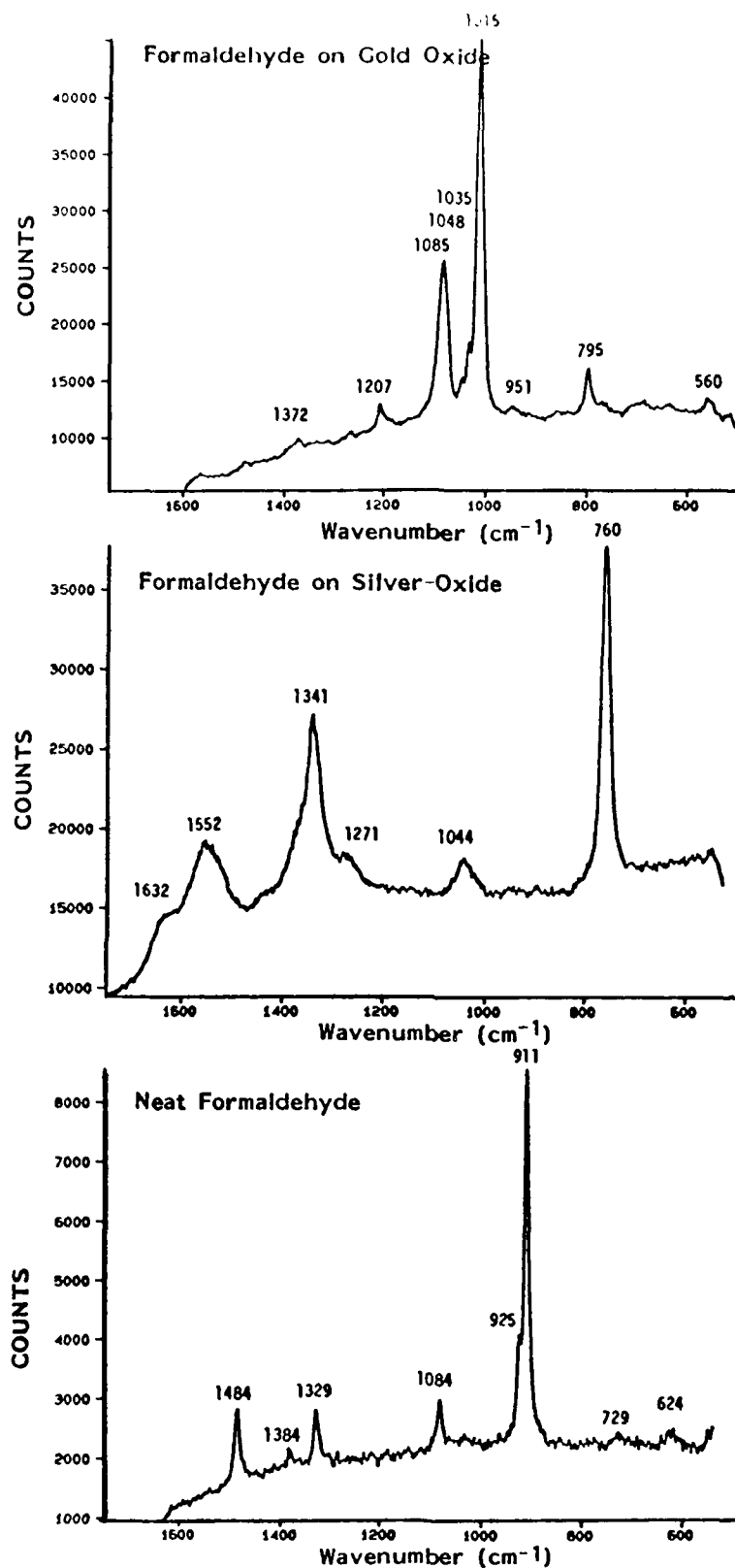


Fig. 9. Normal Raman spectrum of paraformaldehyde (bottom), SERS spectrum of formaldehyde-air on silver oxide (middle) and on gold oxide (top). The excitation wavelength was 575 nm for silver oxide and 625 nm for gold oxide.

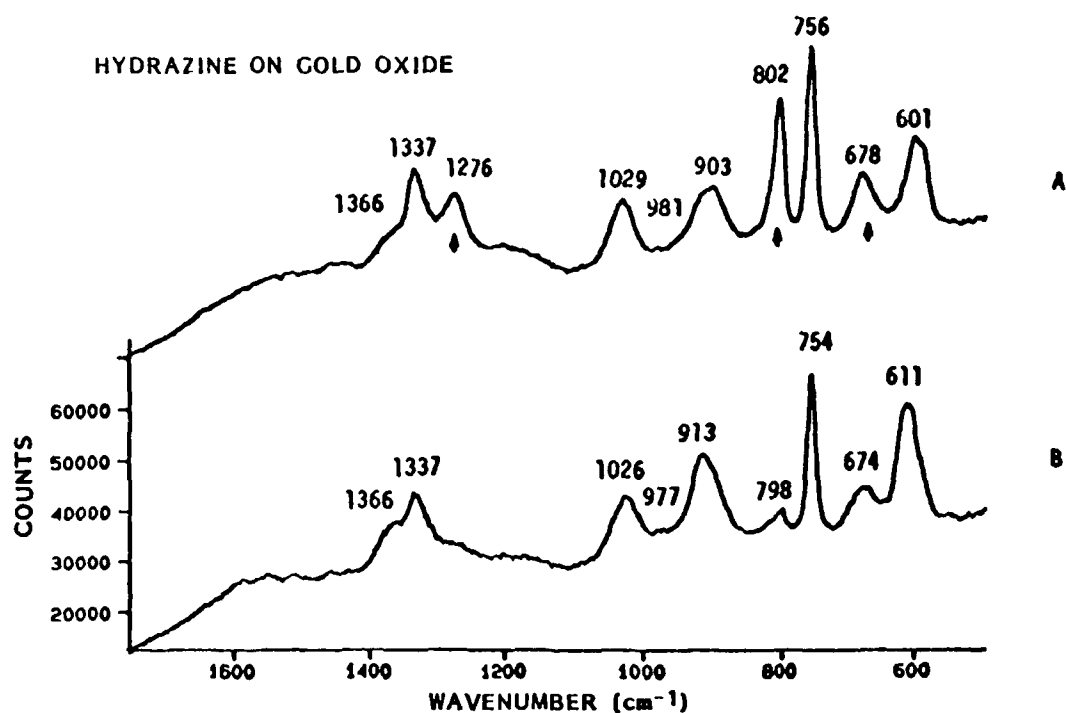
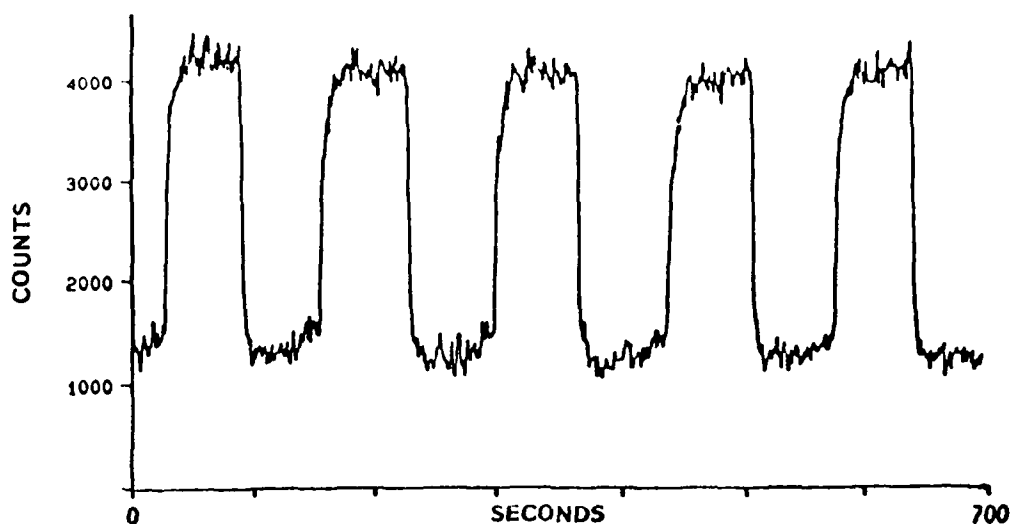


Fig. 10. The SERS spectra (bottom) of hydrazine-air. A) with a 4 ppm flow of hydrazine-air and B) with air purge. Arrows indicate hydrazine peaks. The top curve shows the intensity of the 802 cm^{-1} peak as the sample was alternately switched from hydrazine-air (4 ppm) to air.

We have also observed the SERS spectra of DMMP, a chemical agent simulant, on both silver oxide and gold oxide surfaces. Figure 11 compares the normal Raman spectrum of DMMP with the SERS spectrum on silver oxide. The results show there are at least three peaks (indicated by arrows) that are similar to those of methanol on silver oxide. These may arise from a similar decomposition reaction as occurs with methanol.

The gold oxide again displays a dynamic, reversible adsorption process with DMMP. Figure 12 shows the DMMP spectrum along with a plot of the response of the signal from a major peak to step changes in the DMMP concentration. As with methanol, the response time to reach 90% of the maximum signal is approximately 30 seconds following a step change in the DMMP concentration.

A preliminary study was conducted to determine the dependence of the SERS signal on the vapor concentration. The SERS signal versus concentration curve for pyridine on gold oxide is shown in Figure 13. We were limited by our mixing apparatus to the concentration range of 200 to 2700 ppm. At these concentrations, the response appears to be approaching saturation. However, the data suggest that at lower concentrations (i.e., ppb levels) the signal intensity reflects the concentrations.

Experiments were conducted to evaluate the effect of the carrier gas on the SERS signal of the molecule of interest. Oxygen and nitrogen were investigated since they are the major components in normal atmospheric conditions. Our experiments indicated that neither of the two gases interfere with the observation and resolution of the SERS signal from the molecule of interest.

Experiments were also conducted to test the ability of observing the SERS effect in the gas phase at low laser powers. This was done to test the feasibility of using diode laser and other compact excitation sources. Figure 14 shows the SERS spectra of methanol on silver oxide at various laser powers. It is evident that acceptable SERS spectra can be obtained even at powers as low as 20 mW. This suggests that future instrumentation may be designed using a diode laser in conjunction with highly portable spectrometers.

The resolution of a gas phase mixture of methanol and ethanol has also been observed with the SERS technique. These compounds were chosen to see if molecules with similar structures could be resolved in the gas phase. Figure 15 is the SERS spectra of a gas phase mixture of methanol and ethanol on a gold oxide substrate. Table 1 contains a list of peak positions. It is evident that the vibrational bands of the individual molecules are observable.

The temperature and concentration dependence of the SERS signal observed in some cases indicate where adsorption/desorption is probably an equilibrium process. The adsorption of organic molecules on a metal substrate can be chemically specific due to its free energy of adsorption (ΔG_{ads}). The adsorption of a variety of organic molecules has been evaluated on numerous metal substrates [16]. Considerable variation in free energy, ΔG_{ads} , is seen with organic structures if the reaction is carried out in the gas phase. Figure 16 shows the effect of the ΔG_{ads} on the fractional coverage of the surface. The structural selectivity of adsorption and SERS activation on a metal substrate will be a key issue in employing SERS in the analysis of mixtures.

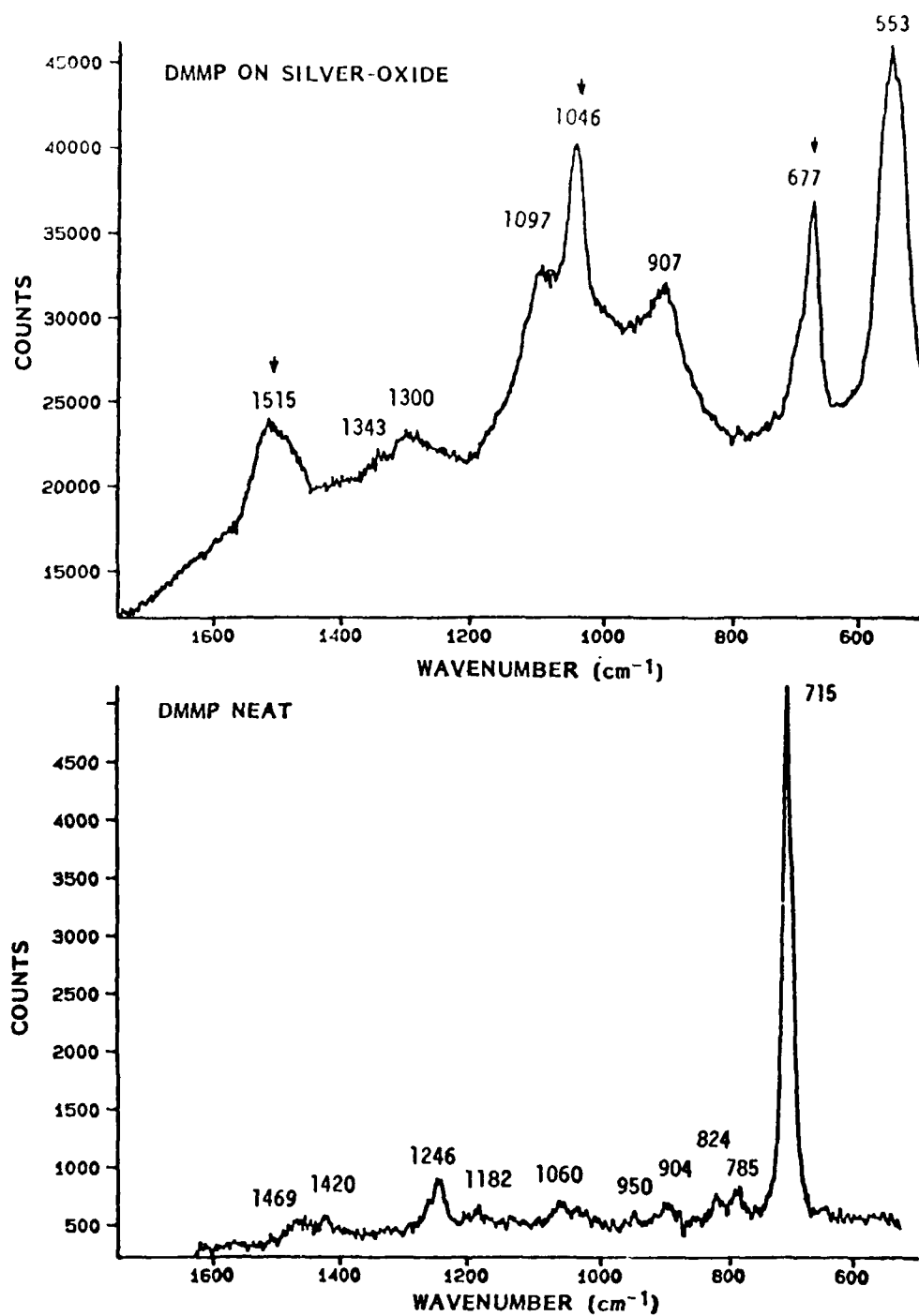


Fig. 11. SERS spectrum of DMMP-air gas samples on a silver oxide substrate at an excitation wavelength of 575 nm (top) and the normal Raman spectrum of a neat DMMP sample (bottom).

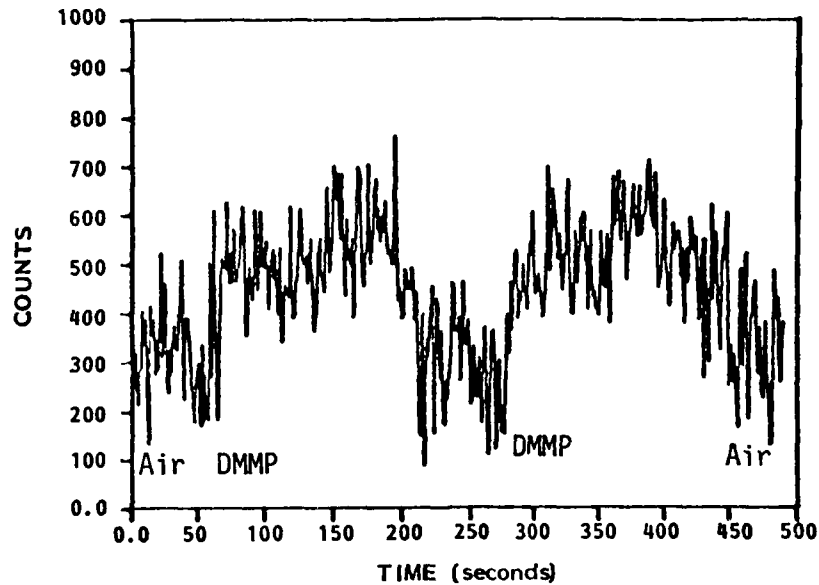
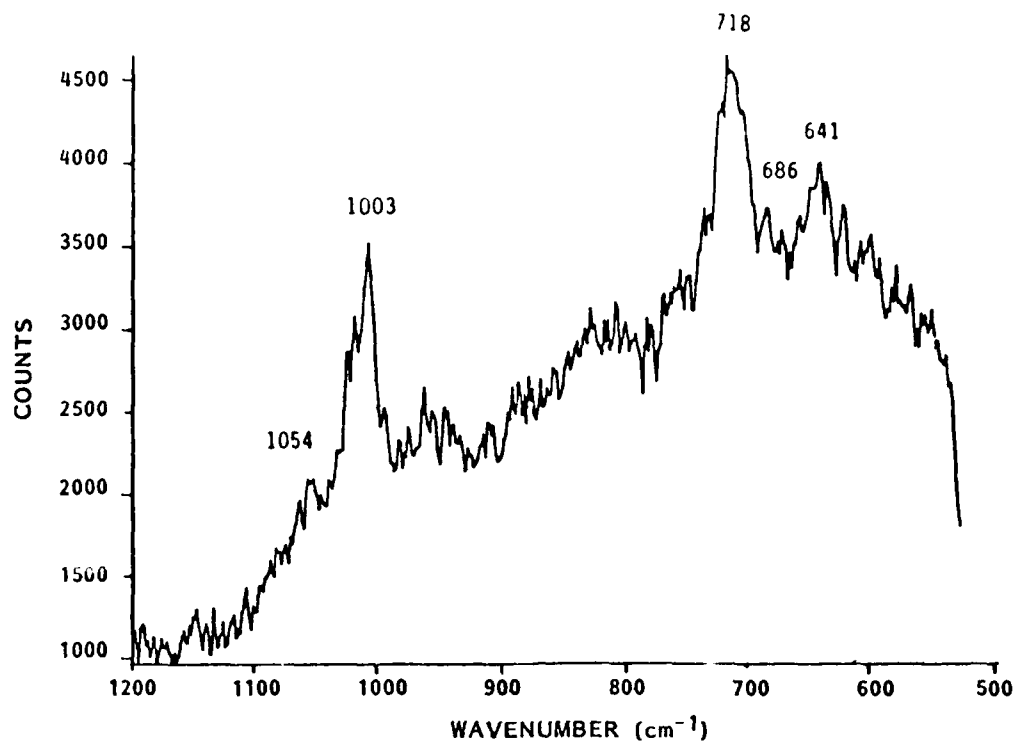


Fig. 12. SERS spectrum (top) of a DMMP-air gas sample on a gold oxide substrate at an excitation wavelength of 625 nm. The bottom curve shows the intensity of the 718 cm⁻¹ peak as the sample gas was alternately switched from DMMP-air mixtures to air.

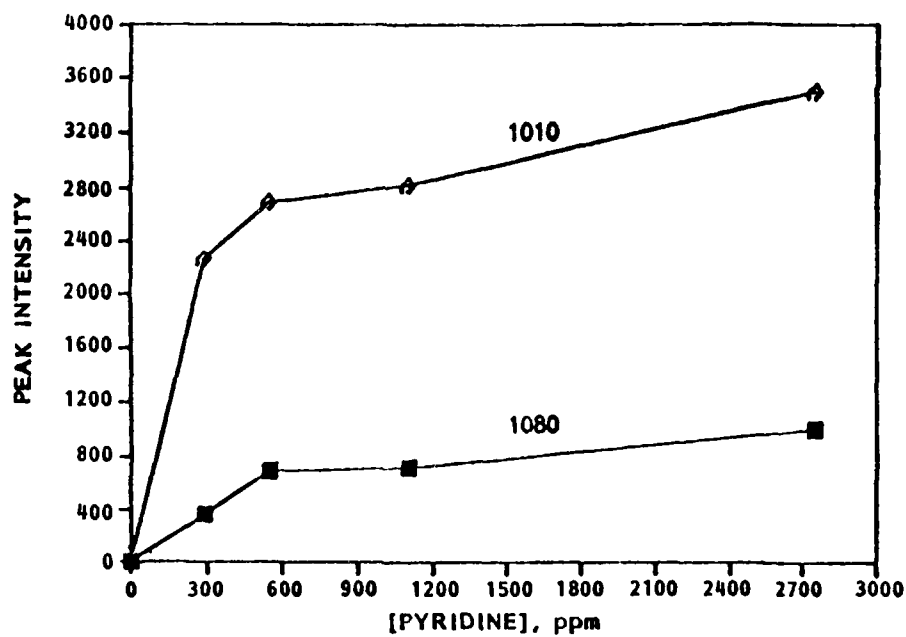
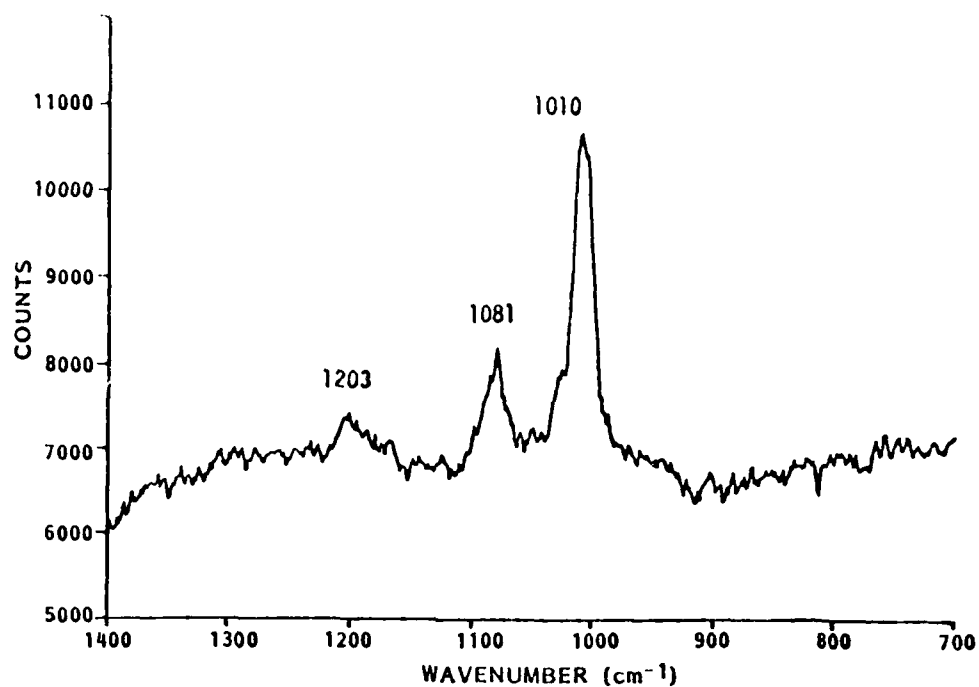


Fig. 13. Plot of the intensity of the 1010 cm^{-1} peak of the SERS spectrum of pyridine on gold oxide as a function of the pyridine concentration in the sample gas (spectrum on top).

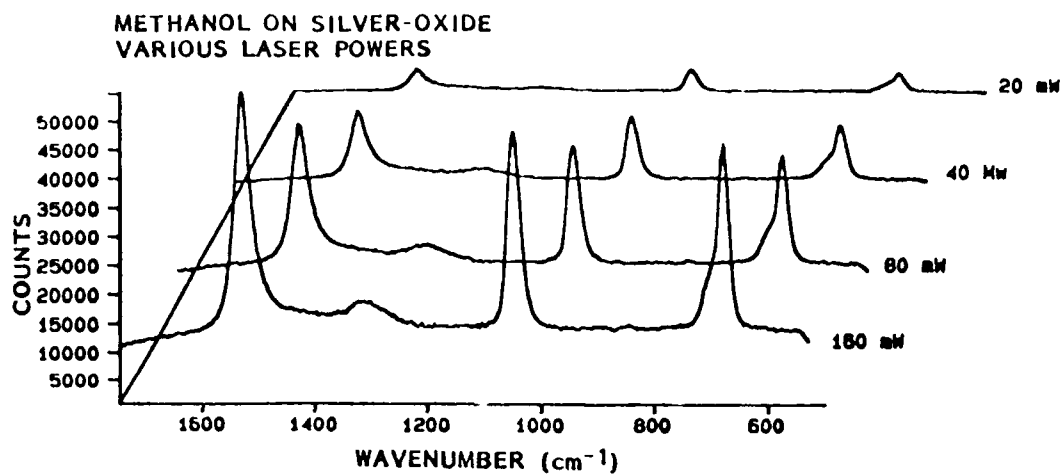


Fig. 14. SERS spectra of methanol on a silver oxide substrate at an excitation wavelength of 575 nm as a function of laser power.

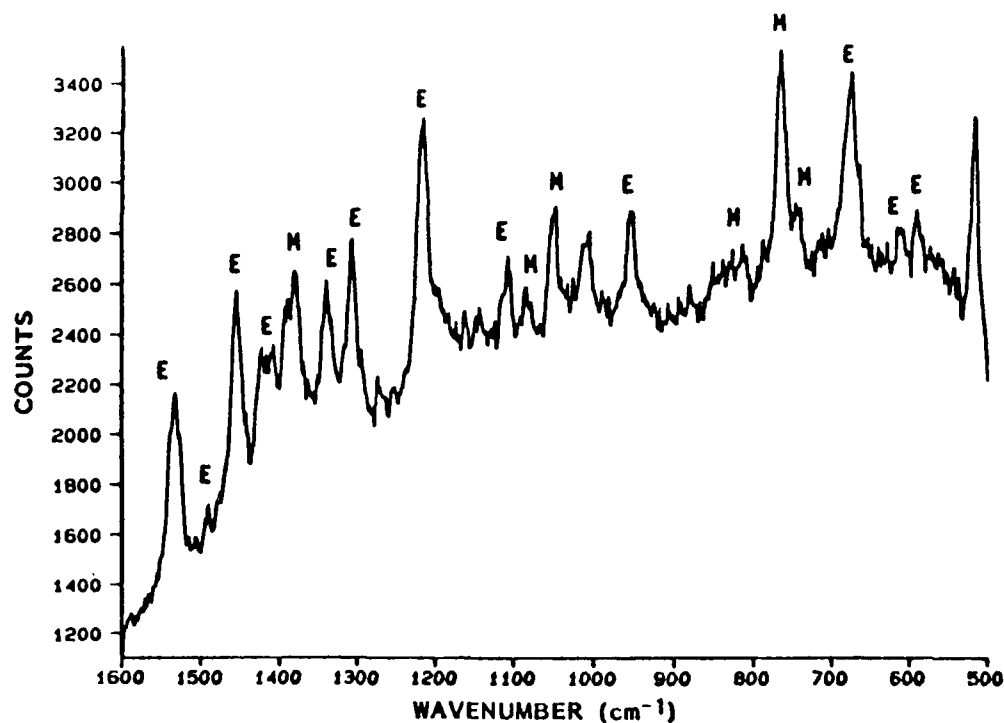


Fig. 15. The SERS spectrum of a mixture of methanol and ethanol in air on a gold oxide substrate. The excitation wavelength was 625 nm and the concentration of methanol was 88 torr while the ethanol was 41 torr.

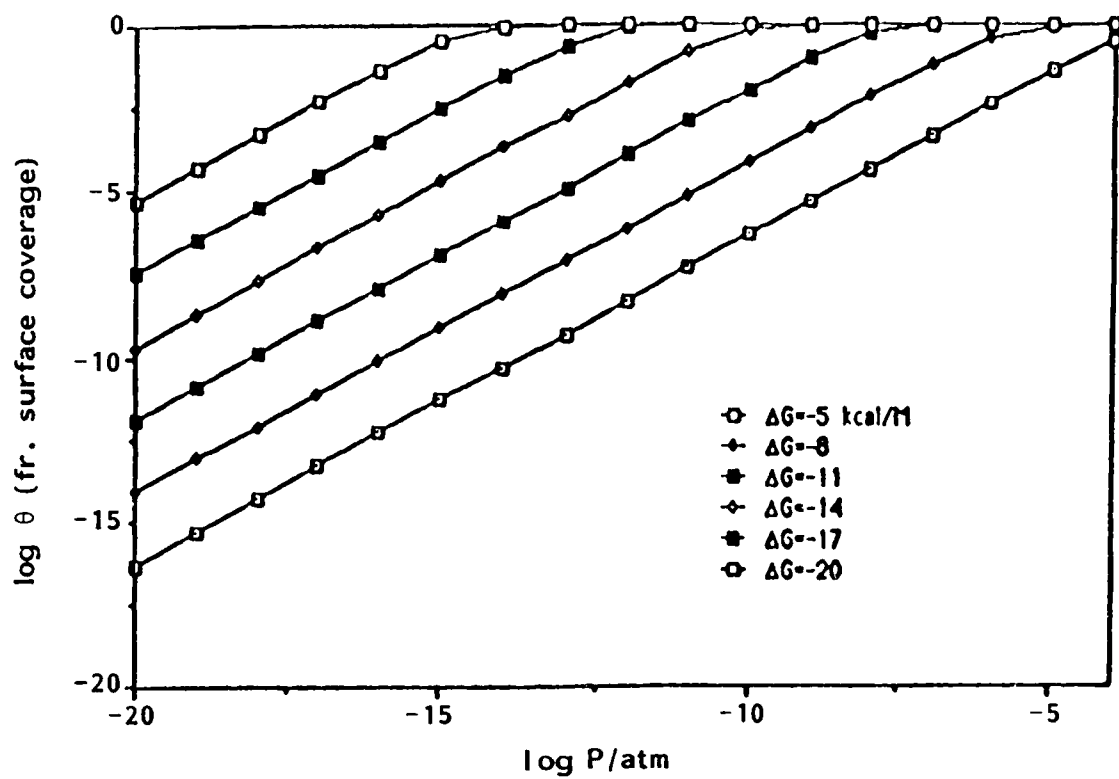


Fig. 16. Calculation of fractional coverage (θ) vs. partial pressure (p) for various free energies of adsorption (ΔG), assuming a Langmuir isotherm.

TABLE 1
PEAK POSITIONS IN cm^{-1} FOR METHANOL, ETHANOL AND A 2 to 1 MIXTURE
(METHANOL/ETHANOL) ON A GOLD OXIDE ELECTRODE

<u>Methanol</u>	<u>Mixture</u>	<u>Ethanol</u>
518	518	521
		571
	592	594
	611	
	676	679
748	748	
764	767	764
	790	
	828	823
882	882	
959	957	959
1007	1007	1007
1050	1050	1050
1077	1085	
1108	1107	1110
	1144	
1158	1162	1168
1216	1216	1216
1270	1273	1270
1306	1306	1309
1342	1339	1339
1379	1379	
	1390	
1408	1408	
	1422	1418
1456	1454	1456
	1475	1475
1533	1533	1533

One of the overall objectives of the program is to configure SERS for remote fiber optic excitation and detection. Although our gas phase cell in Phase I was not constructed for fiber optic applications, independent work has been carried out in our laboratory on fiber optic probe design [17]. The probe was constructed to contain a 100 μm excitation fiber surrounded by four 600 μm collection fibers. Output from the latter was imaged onto the monochrometer slit. Figure 17a shows a SERS spectrum of pyridine on Ag in which excitation and collection was accomplished via the 2 meter fiber optic bundle. Although the spectrum of pyridine is clearly observed, there is a background in the 500 to 900 cm^{-1} region due to Raman scattering from the silica delivery fiber itself (Figure 17b). The computer corrected spectrum obtained from subtracting the background is shown in Figure 17c.

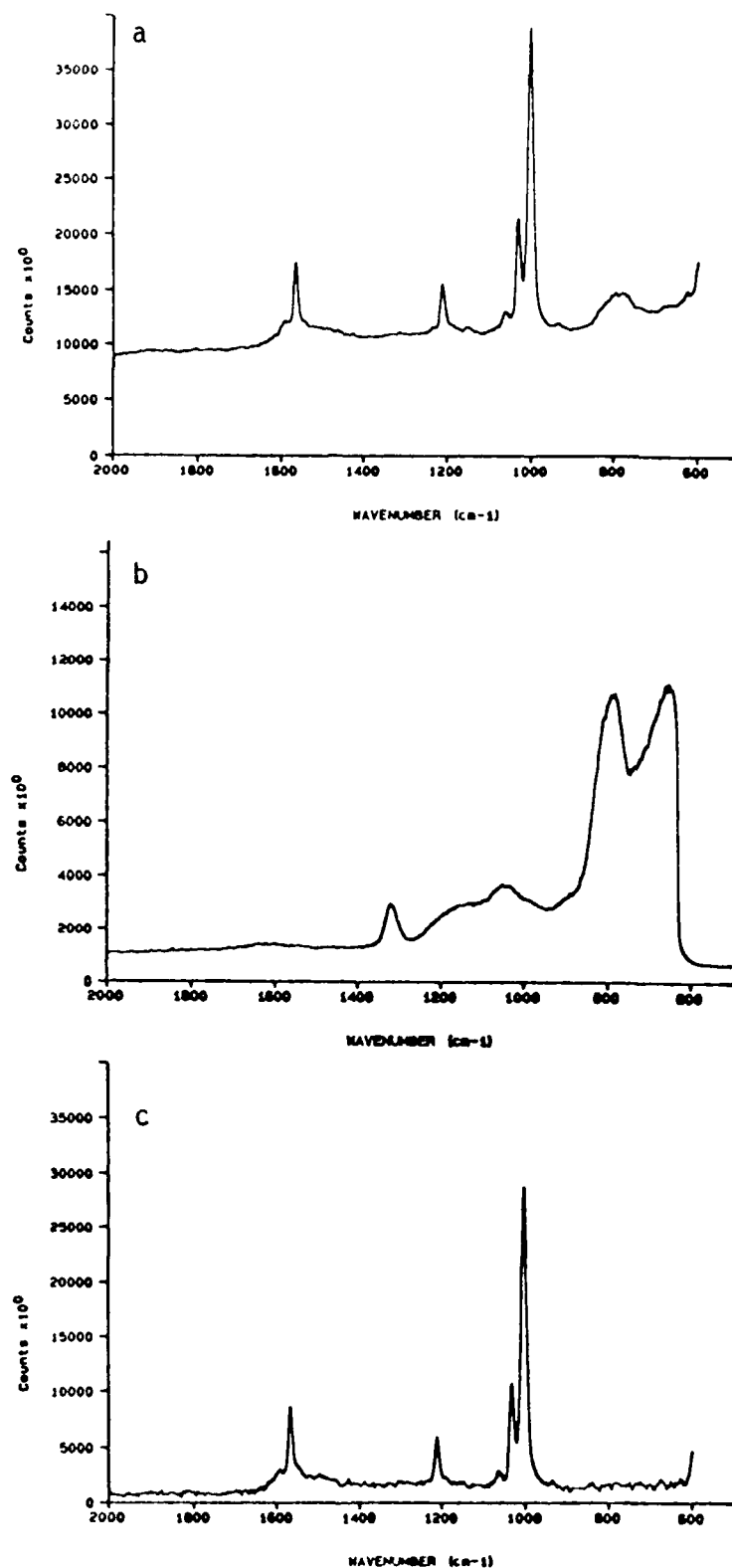


Fig. 17. a) Fiber optic SERS spectrum of 0.5M pyridine in KCl electrolyte. The electrode potential was -0.6V and the excitation wavelength was 514.5 nm; b) Raman scattering of silica induced in the excitation fiber optic; c) SERS spectrum after the subtraction of the background silica signal.

SUMMARY AND CONCLUSIONS

The results of the Phase I experiments on gas phase SERS are summarized in Table 2. It may be concluded that the oxides of Ag and Au give rise to SERS activity for gas phase adsorbates, while such activity is generally lacking for the metal substrates alone. This activity is observed in air, with no apparent interference from simple atmospheric gases. The gold oxide surface shows the most promise of supporting dynamic, physisorptive equilibria, although strong chemisorption and irreversible reactions on Ag oxides could be utilized for high sensitivity. Phase I results are promising in establishing discrimination of molecular functionalities using different substrates, particularly with the use of SERS-active metal oxides. It is likely that oxides can be further modified by ion exchange or covalent bonding to impart additional degrees of structural selectivity. Renewal of substrates has been demonstrated by simply changing the solution concentration of adsorbate or increasing substrate temperature, or by electrochemical ORC. Finally, we have shown that Raman spectroscopy can be conducted using silica optical fibers as delivery and collection systems.

TABLE 2
SUMMARY OF GAS PHASE SERS RESULTS

	Ag	Ag ₂ O	Au	Au ₂ O ₃	Cu
Pyridine	Y ¹	N	Y ²	Y ³	Y
Methanol	N	Y	N	Y ¹	-
Ethanol	N	Y	N	Y ¹	-
Formaldehyde	N	Y ⁵	N	Y ⁵	N
Benzene	N	N	Y ¹	Y ⁴	N
DMMP	N	Y ⁵	N	Y ¹	-
Toluene	Y ¹	N	Y ²	-	-
Hydrazine	N	Y ¹	Y	N	-

¹SERS at 20°C, desorbed if flow changed to air.

²Desorbs with heating.

³Thermally desorbs at 80°C.

⁴Thermally desorbs at 54°C.

⁵Reacts with oxide on heating.

Presently, no remote fiber optic chemical sensor exists for the analysis of organic compounds in both gaseous and liquid environments which has both the sensitivity and universal selectivity of the SERS technique. The SERS technique would serve as a continuous monitor for organic compounds and would allow the real time qualitative and quantitative analysis for a wide variety of industrial and military applications. These applications include the areas of robotics, hazardous waste monitoring, chemical warfare, environmental control of cabin atmospheres (i.e., ships, submarines, planes, tanks, etc.)

and in process control monitoring. Process control monitoring could include the area of electronic fabrication of devices where precise control of the environment is critical.

In order to address these applications, future work will be directed both at developing SERS substrates for gaseous and liquid environments and also compact and robust Raman instrumentation for field use. The further development of fiber optic SERS will be critical for remote sampling, necessary for many of the proposed applications.

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